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Waste-Gas Temperatures of Rotary Kilns.

THEIR PRECALCULATION AND THE PREDETERMINATION OF FUEL CONSUMPTION AND EFFICIENCY.

By Dr.-Ing. Rudolf Frey.

THIS work is the result of a suggestion made by Miag Mühlenbau- und Industrie A.G., of Braunschweig, to whose Director (Herr Bergen) I am particularly indebted in this connection. The carrying through to the required accuracy of the experimental figures necessary for the computation would not have been possible without the numerous test results and the assistance accorded me by this firm.

Introduction.

With all the advantages of the rotary kiln from the standpoint of operation and quality of burning, it has had from the start the disadvantage of a high heat consumption. With large-capacity kilns, the question has arisen how this fault can be eliminated and what proportion of the heat expended is really necessary for the manufacture of cement.

All tests to find this theoretical amount of heat were useless if based on heat balances. For even had it been possible to give approximately, through accurate determination, the absolute values for the losses by radiation and convection from the kiln and cooler shells, there was no method of predetermining the exit-gas temperature of the kiln and so determining one of the main factors of the heat requirement, namely, the losses in the waste gases.

Tests made up to the present determined only the heat requirements for the intended physical or chemical reaction and found the losses as balances without being able to show their theoretical necessity. For this reason they did not accurately describe the efficiency of the rotary kiln because they did not show what heat consumption would be sufficient under the most favourable conditions.

The question as to the fuel consumption should not be " How much coal is necessary for the transformation of one ton of material to be burned ? " It should be " How much coal is required for operating the kiln per ton material to be burned ? "

The duty of a kiln is the maintenance of a certain required temperature, and is therefore simply the counterbalancing of a heat loss consisting mostly of several single items. In this sense, also, the heat required for chemical reaction in the kiln is not an item fundamentally different, but losses and heat required for such chemical reaction form together the heat required which is supplied by the cooling of the gases from their maximum combustion temperature to the exit-gas temperature. This drop in temperature determines the amount of combustion gas which must be developed to cover this requirement, and therefore the fuel consumption, and the efficiency of the kiln can be measured by a comparison of the total available reduction of heat between the maximum temperature and the zero point.

Friedr. C. W. Timm attempted in 1906 to solve mathematically and physically the problem of exit-gas temperature by examining the conditions of the temperatures and the heat transition along the shell of the rotary kiln. He used as the basis a curve of the elimination of the carbonic acid over the length of the kiln, but this curve is not reconcilable with the results of new tests obtained in the laboratory. Even if one accepts the basis (although it is partly incorrect) on which the calculations of Timm are based, one does not get with their help any general idea as to directions in which the rotary kiln may be improved. The calculation cannot be used to give in advance accurate figures of fuel consumption of a rotary kiln of certain dimensions, or to ascertain the relative importance of the various influences by which fuel consumption is affected.

The method of mathematical and physical examination of the problem attempted by Timm has therefore been abandoned, and a more empirical mode of calculation has been used which, originally worked out for rotary cement kilns, can also be applied for the burning of lime and may be readily adapted to other burning processes and special kilns. By this new method of calculation for determining waste heat losses, the losses by radiation from the walls of the rotary kiln are ascertained together with the waste-gas temperature, and no further difficulties are experienced in the determination of fuel consumption if use is made of a suitable form of heat balance. Throughout the calculation it will be found that even an insulated kiln, i.e., one without losses by radiation and conduction, requires a certain waste-gas temperature, and that one may therefore only designate as kiln efficiency the relation between the actual thermal efficiency and the ideal one of the insulated kiln. Every rotary kiln has a thermally conditioned maximum output the relation of which to the actual output provides a useful comparison of different kilns. Finally, the calculation permits a verification of the influence of structural or operating changes on the rotary kiln, and a judgment as to its latest development.

Determination of Waste-gas Temperature.

The heat transmission conditions in the interior of the rotating tube decide the temperature of the waste-gases with which a given kiln must work, and the method of determining the temperature of the waste-gas is as follows. On account of the temperature difference existing between the kiln gases and their surroundings, the heat of the gases passes through the limiting surfaces of the gas stream, i.e. the surface of the material to be burned and the free inner surface of the kiln, In the intensity of this transmission there are considerable differences, depending on the nature of the surrounding kiln gas. While the transmission of the heat necessary for the evaporation of the moisture in the fuel offers no difficulties on account of the good heat exchange between gas and water, the transmission of the heat to the dry material to be burned and to the firebrick lining is difficult, so that with a given kiln surface and a given maximum gas temperature only a

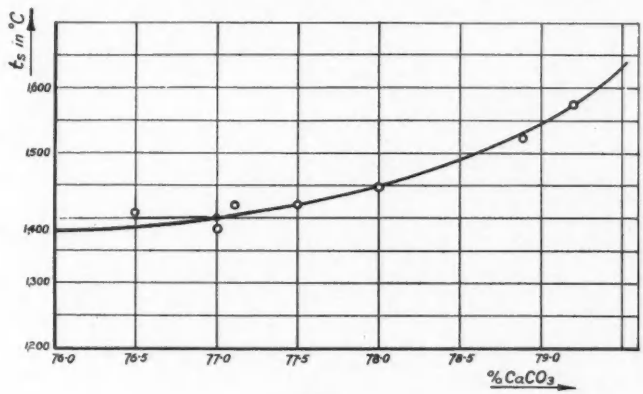

Fig. 1.

limited quantity of heat per hour per ton of material, dependent on the waste-gas temperature, is available. If the sum of these items required per ton of material is determined the waste-gas temperature can be calculated from an equation in which the available and the necessary heat are balanced.

It is not possible to calculate the heat exchange proceedings sufficiently accurately with the help of fundamental constants. It is therefore necessary to determine heat transference and heat exchange factors as comprehensively as possible from test results and then precalculations are possible. For the correctness of the results exactly the same simplifications and rules must be considered in the precalculation as in the determination of the necessary factors. Although the calculation is limited in its range of validity through these auxiliary factors, it is only a matter of tests to ascertain the validity of the calculation which in the following is related to the manufacture of cement.

Waste-gas temperature and kiln-shell losses are obtained from the co-ordinates of the point of intersection of two curves, the curve of heat required and the

kiln gas heat curve, both of which are calculated for several waste-heat temperatures, assuming a constant standard output of the kiln. The curve of heat required indicates the sum of the amounts of heat per ton of material which must be transferred to the dry raw material (without moisture content) and to the kiln lining, while the gas heat curve denotes the heat per ton of material to be burned, which is available between the theoretical combustion temperature and the waste-gas temperature from combustion. The intersection of the curves shows the waste-gas temperature at which there is equilibrium between available and necessary heat. At the same time there results the kiln shell loss of this waste-gas temperature.

HEAT REQUIRED.—The ordinates of the heat curve required are composed of three sections: (1) Heat required for the chemical or physical transformation of the material to be burned, (2) heat required for heating the material to the temperature necessary for (1), and (3) Heat required for covering the heat losses from the rotating tube by radiation and convection. The first two items form a constant requirement independent of the waste-gas temperature, while the third item, the shell losses, is dependent on the waste-gas temperature.

The constant requirement for (1) and (2) is easily obtained because the necessary figures for the temperature ranges and the specific heats are known particularly well for the cement industry. Numerous calculations have led to the following results:

The heat necessary for driving off the carbonic acid from the calcium carbonate of the raw meal is (−425) kcal. per kg. $CaCO_3$, and that for driving off the carbonic acid from the carbonate of magnesium is (−215) kcal. per kg. $MgCO_3$. From the total of these is subtracted the heat to the amount of 100 kcal. per kg. cement clinker liberated by the exothermic reaction during clinkering.

For heating the dry raw meal from the feed temperature to the temperature of 950 deg. C. necessary for the decomposition of the carbonates, its specific heat is taken as 0·21 kcal. per kg. per deg. C. according to Wecke, while for the further heating of the mass of clinker the mean specific heat with the value of 0·25 kcal. per kg. per deg. C., given by the same author, must be taken.

For the determination of the clinkering temperature the widely divergent figures of the literature could not be used, while a strictly theoretical determination is not possible on account of the variety of the calcium and calcium-aluminium silicates present. It was therefore decided to give on a curve the maximum temperatures of the material being burned measured on the most diverse kilns as a basis for precalculations. Although the temperatures were not found by the same measuring methods, on plotting them over the $CaCO_3$-content of the raw meal there resulted the curve shown in Fig. 1, which has proved very useful for precalculations. The range of the points lies inside the limits admissible for the accuracy of the calculation. Differences in the fineness of the raw meal and inaccuracies of the measurements no doubt account for the divergences.

The fineness of grinding of the raw meal lay between 0·8 and 2·5 per cent. residue on a sieve of 900 meshes per sq. cm. and between 10·0 and 12·0 per cent.

residue on a sieve with 4,900 meshes per sq. cm. In this range lie the usual finenesses of grinding, for which the curve is therefore applicable.

(3) For the measurement of radiation losses the mean interior temperature of the brick lining is required, and it is therefore necessary to find an approximate formula to give this temperature. The maximum temperature of the material burned and the temperature of the waste gas mainly influence the height of this mean interior temperature, while the influence of the theoretical combustion temperature and of the temperature of the raw material on entering is less. The determination of the course of the temperature in the interior of the kiln by measuring the temperature and deducting therefrom the mean interior temperature has not been made use of because an approximate formula is of more general validity than a determination deduced from such measurements, particularly as slight inaccuracies which arise in the use of an approximate formula are eliminated by the method employed in using the present test figures.

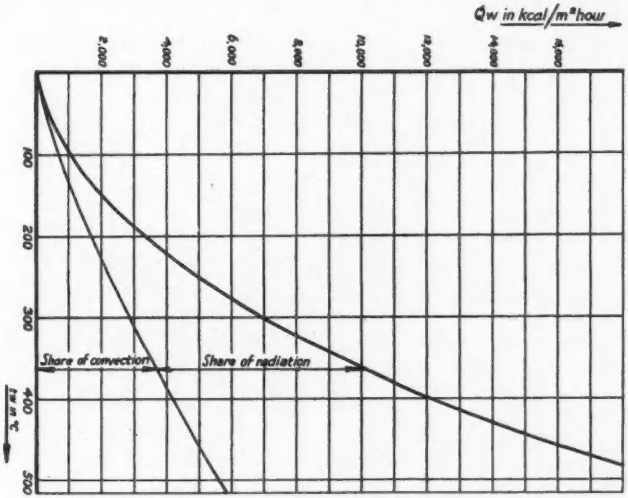

Fig. 2.

For coupling the two decisive temperatures (the maximum temperature of the material burned t_s and the waste-gas temperature t_g) three formulæ have been taken into consideration:

(1) The arithmetic temperature mean

$$t_{i1} = (t_s + t_g) \div 2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

(2) The mean logarithmic difference of the temperature against the exterior t_a.

$$t_{i2} = \frac{t_s - t_g}{ln\,(t_s - t_a) - l_n\,(t_g - t_a)} + t_a \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

(3) The logarithmic mean of the absolute temperatures

$$t_{i3} = \frac{T_s - T_g}{ln\,T_s - ln\,T_g} - 273 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

With the temperatures according to these equations the mean thermal conductivity coefficients for the shell of the kiln were computed in reverse order for eight rotary cement kilns whose temperatures and heat losses had been measured; the equation used as a basis for the definition of the mean thermal conductivity coefficient was

Shell loss per m^2 per hour $= Q_w = \lambda/\delta\ (t_i - t_w)$ .. .. (4)

The curve in Fig. 2 of the emission of heat from the kiln at different shell temperatures, which is based on the generally known formulæ for radiation and convection, has been used. For each shell loss per square metre per hour determined from the heat balance of a kiln the curve gives the corresponding mean shell temperature of the kiln, and with its help one is able to compute for the mean thickness of shell δ and the mean interior temperature t_i the thermal conductivity coefficient according to equation (4). The figures of this calculation are given in an appendix to be given at the conclusion of this series of articles.

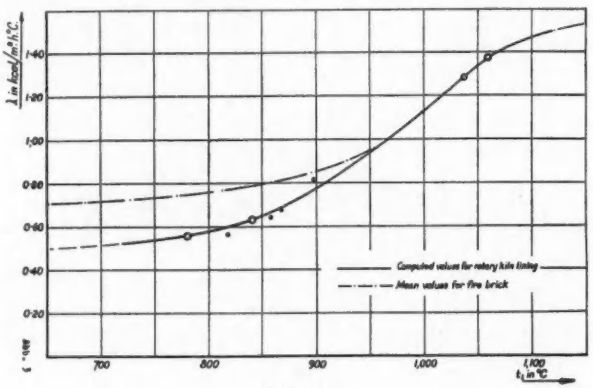

Fig. 3.

From a number of very divergent figures of heat conduction from the literature and from other sources a curve of mean values was fixed for fireclay clinker coating, other influences of the cement-burning operation not being considered. The comparison shows good agreement, particularly of the values computed according to equation (3), in the order of quantity as well as in the lawful course of the curve. The curves obtained with these figures are shown in Fig. 3.

The figures computed with the help of equation (1) were throughout too low, while the equation gives too high mean interior temperatures; equation (2) gives low exit-gas temperatures and too low values for the interior temperature. The following are figures on which the curves in Fig. 3 are based.

With equation (3) the following values were obtained:

t_i = deg. C.	780	817	840	857	866	897	1,037	1,059
λ = kcal. per m^2 m.h. per deg. C.	0·550	0·558	0·621	0·635	0·668	0·809	1·280	1·370

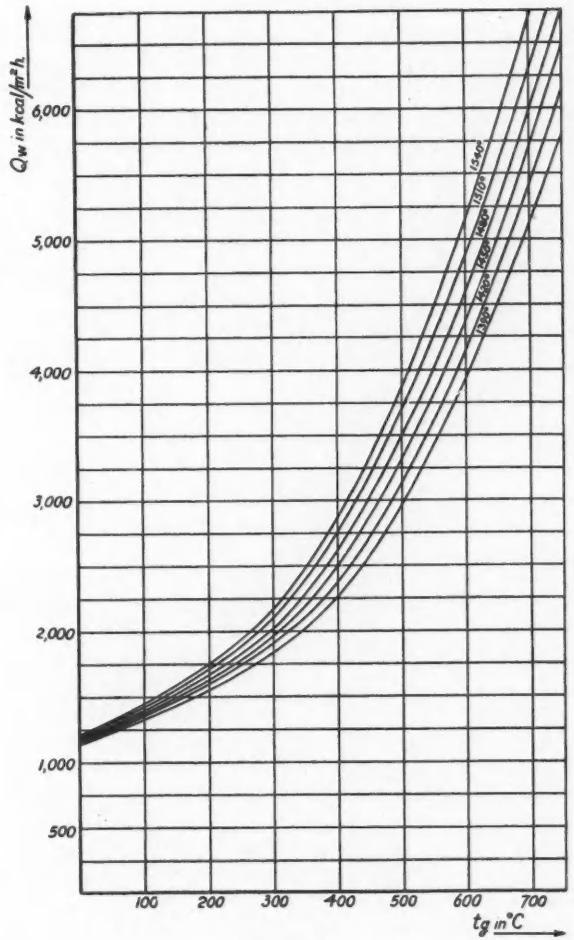

Fig. 4.

For fireclay there were given:

for t_i = deg. C.	400	600	800	1,000	1,200
Max. value: kcal. per m^2 m.h. per deg. C.	0·87	0·97	0·97	1·44	2·98
Min. " " " " " "	0·40	0·44	0·47	0·75	1·00
Mean " " " " " "	0·60	0·69	0·75	1·13	1·57

With the help of the curves of the heat conductivity figures given in Fig. 3 and equation (3) for the mean interior temperature there can now be determined

the value of the shell loss on the kiln depending on the waste-gas temperature necessary for the precalculation. For various selected waste-gas temperatures the mean interior temperature t_i is computed with the aid of equation (3). If now for various t_i the values of Q_w are determined with equation (4), and the straight lines obtained are drawn on Fig. 2, the mean exterior shell temperature over the whole length of the kiln and the shell loss per square metre per hour are found. This lengthy calculation can be avoided with the help of curves using as basis a normal average thickness of kiln lining. The shell losses for each square metre per hour can then be shown by curves directly dependent on the waste-gas temperature, each curve being related to a certain clinkering temperature, so that the intermediate values can be easily found by interpolation. Fig. 4 shows the result of this calculation for an average thickness of lining of 17·5 cm.

The determination of the shell losses for plotting the curve of heat required is then reduced to the shell loss for each square metre per hour taken from Fig. 4 for the various exit-gas temperatures and reduced to the number of kg. material to be burned, taking into account the area of the outer surface of the kiln and the output per hour.

In connection with this calculation is the question whether the differences between the computed and the indicated mean values of the heat conductivity figures, particularly with low mean interior temperatures, can be explained by differences in the quality of the lining of the kiln or by peculiarities of the burning process. A clear decision on this question was not possible because the cost of a test would have been too great; however, it is probable that the deviation in the curves is caused by the fact that the mean value curve is strongly influenced by lining material of lower quality at low temperatures.

For the validity of the curves on Fig. 4 the use of high-class fireclay over as large a part of the kiln as possible is necessary. Control calculations have shown agreement between the figures of this calculation and test results also for kilns for burning lime, gypsum and clay.

FLUE-GAS HEAT.—For flue-gas heat a curve has been defined which indicates the amounts of heat which are available from the flue gas per kg. of clinker for a maximum theoretical combustion temperature at different waste-gas temperatures. If there is an hourly available amount of heat from the heat exchange of the flue gas to the surroundings, this heat can be easily converted to kg. of material to be burned by division with the output per hour, and it is therefore necessary to establish this amount of heat available per hour.

As in similar cases of heat transmission, this amount of heat is dependent on the size of the surface of transmission F, of the difference in temperature Θ, and on a coefficient of heat transmission k in the form

$$Q = \int_0^l k \cdot \Theta \cdot dF \qquad (5)$$

The difficulty is then encountered that k as well as Θ, and eventually also F, change with the distance l of the material being burned from the inlet of the kiln, and that accurate information would have to be given beforehand on the nature of this change.

Even if it were possible to obtain this information with the help of approximations the calculation would become too lengthy for practical purposes, and at the same time new uncertainties would be brought into the calculation which would defeat the object in view. The value of the integral may, however, be determined much better from test results by writing

$$Q = {}_0\int^{l} k \,.\, \Theta \, dF = m \,.\, \Theta_m \, F_i. \qquad .. \quad .. \quad .. \quad .. \quad .. \quad (5a)$$

Where m denotes an auxiliary value computed from the test figures, called the coefficient of the exchange of heat,

Θ_m is the mean effective temperature difference between the flue gas and the material being burned, and

F_i is the interior surface of the kiln lining.

In this application the question arises under which hypothesis the auxiliary value m, computed in this manner for cement kilns from test data, can be used for the precalculation of other kilns and which influences would necessitate a correction. If, as in the empty kiln, heat were transmitted only to the lining and spread from there, the heat transmission conditions would be always the same with the same fireclay and temperatures, and there would be no objection to the use of the figure found for m. Corrections can only be required because of the material in the kiln.

The material being burned differs thermally from the lining less in the thermal conductivity and the specific heat of the particles than in the amount of free interstices. These interstices reduce the heat conductivity in the interior of the heap of material being burned, and the reduction of the heat conductivity increases as the weight per litre decreases. Although the continuous movement of the material counteracts this, the material acts more as an insulator than the fireclay (part of the heat transmitted to the material comes from the hot lining), and this influence is greater when there is a greater charge in the kiln.

As the load in cubic metres in the kiln is affected by the slope of the kiln and its speed, the following possibilities of error may arise through this application: (1) Influence of the output per cubic metre, (2) influence of the slope and speed of the kiln, and (3) influence of the granulation of the raw meal (weight per litre).

Various values from a number of heat balances resulting in the calculation of m were used to ascertain the amount of these influences, and it was found that the error becomes noticeable only in cases of very exact calculations. There resulted in one case with $m = 33{\cdot}2$ instead of $32{\cdot}7$ a heat required of 1,435 kcal. as compared with a consumption of 1,480 kcal. measured during the test, and in another case with $m = 33{\cdot}2$ instead of $35{\cdot}0$ a heat required of 1,670 kcal. instead of 1,641. The errors are therefore within permissible limits.

The figure to be used for m can only be obtained after the two other factors of equation (5a), F_i and Θ_m, have been decided.

The internal surface of the kiln (F_i) must be computed from the dimensions, giving consideration to the mean thickness of the lining. It must be noted that chains and similar devices inside the tube would increase the kiln surface, and

the effect of these has to be determined by test. From comparison between kilns with and without chains an idea is obtained as to the extent of their influence, and it could be determined that for each metre length of kiln provided with chains the internal surface of the kiln increased by about the size of a section of the kiln..

The fluctuation of the temperature differences according to the length of the kiln is taken into consideration by calculating the logarithmic mean from the maximum and minimum temperature differences occurring:

$$\Theta_m = \frac{\Theta_{max} - \Theta_{min}}{ln\Theta_{max} - ln\Theta_{min}} \quad .. \quad .. \quad .. \quad .. \quad (6)$$

The temperatures to be used for determining these differences are

Maximum theoretical combustion temperature .. t_{max}
Maximum temperature of the material being burned.. t_s
Temperature of exit gas .. .. t_g
Feed temperature of material .. .. t_e

so that the following formula is obtained for the mean temperature difference.

$$\Theta_m = \frac{(t_{max} - t_s) - (t_g - t_e)}{ln(t_{max} - t_s) - ln(t_g - t_e)} \quad .. \quad .. \quad .. \quad (6a)$$

There is a slight inaccuracy in using equation (6*a*) as it is valid for the mean effective temperature difference in heat transmission in continuous current, counter-current and cross-current, but here the course of the temperature curves may be changed by heat-consuming or heat-producing processes in the material being burned. Nevertheless, the formula is a good approximation, because these influences on the course of the temperature remain small.

Respecting formula (6*a*), the maximum theoretical combustion temperature t_{max} has a special influence on the waste-gas temperature and therefore on the fuel consumption.

The temperature increase taking place in the combustion of the fuel is determined in the usual manner from its calorific value and from the weight of the flue gas developed during combustion. For low-grade coal an elementary analysis is also necessary. However, for the kinds of coal dust principally used in rotary cement kilns the formula for the weight of the flue gas given by Brauss for the calorific value of pure carbon may be used for simplification in the form

$$L_{th} = 0.00143 . H_u \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

$$G_R = l + \epsilon . 0.00143 . H_u \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7a)$$

in which

L_{th} = minimum weight of air per kg. coal
G_R = weight of flue gas per kg. coal
H_u = net calorific value per kg. coal
ϵ = amount of excess air.

From this results the heat-content per kg. of flue gas (without preheating the air):

$$H_u/G_R = \frac{H_u}{l + \epsilon . L_{th}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (8)$$

To this is added the heat-content of the combustion air on entering the kiln, and from the sum of these amounts follows the corresponding theoretical combustion temperature.

The coal fired in the kiln under examination had an average of 75 per cent. carbon, 5 per cent. H_2, 9 per cent. $O_2 + N_2$, 1 per cent. sulphur, and 10 per cent. ash.

For the precalculation the excess of air and the temperature of the air must be known, and it is here best to use standard figures as a basis. In cement burning the theoretical combustion temperature may reach nearly the limit imposed by the resistance of the lining. This is about 2,200 deg. C. This is only possible with a small excess of air and a high pre-heating temperature. The kilns with air seals which were examined had been running with an excess of air of 1·10 or less except in one case with 1·16, and it is reasonable to assume 1·10 as a standard figure. A skilled burner can maintain excesses of air of 1·09

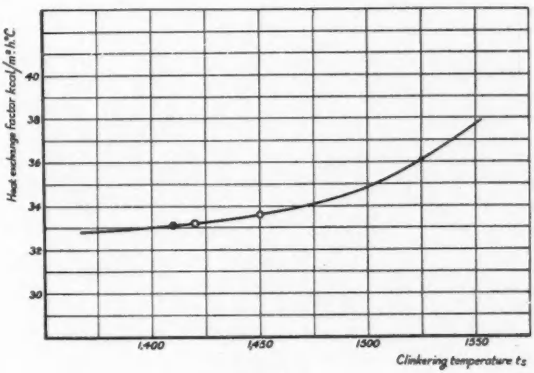

Fig. 5.

and 1·08 in continuous operation without too much CO being contained in the exit gases; with these excesses of air the clinkering time has been adequate and the burning of the clinker perfect.

To obtain a theoretical combustion temperature of 2,200 deg. C. with an excess of air of 1·10, the combustion air would have to be preheated to about 400 deg. C. with a normal coal of about 7,000 kcal. net heating value. With full use of the heat contained in the clinker at about 24 per cent. fuel consumption, this would be possible. Accordingly, in the rotary cement kiln using bituminous coal dust, a maximum theoretical temperature of 2,050 to 2,100 deg. C. is obtainable by correct dimensioning of the cooler and proper operation.

The necessary preheating of the combustion air depends on two factors, (1) the relation of the primary air to the secondary air, and (2) the losses of the cooler. The primary air with which the coal dust is injected is usually not heated above 60 to 80 deg. C., while, according to the type of cooler, the secondary

air may have a temperature of 300 to 500 deg. C. In the cases examined in practice, about 35 to 42 per cent. of the entire air is introduced as primary air and therefore only 48 to 65 per cent. of the air is preheated. The correct proportions of primary and secondary air depend on the conveying of the coal dust and the coal-feed pipe must be of a suitable size. The steps of this calculation are explained in the appendix.

The temperature of the secondary air depends to such an extent on the construction of the cooler and on the operation of the kiln that each type would have to be considered separately. In general, the cooling drums must not be too small, so that the heat losses on the cooler remain small and as much heat as possible is transmitted directly to the secondary air. Such coolers are more efficient than coolers without insulation and the radiation of the cooler is employed for preheating the primary air, because the greater part of the heat is lost again in the pipelines to the fan, which in most cases are very long. In this respect the cooler arranged in prolongation of the kiln is an improvement, very small heat losses being obtained, so that higher theoretical combustion temperatures than 2,100 deg. C. would be obtainable with it.

In spite of the use of high-grade fireclay for the lining there is always a risk in prescribing higher maximum temperatures for continuous operation and for this reason the standard figures already mentioned were fixed.

After the definition given the heat exchange figure m can be determined from test measurements on the kiln if complete heat balances are computed from the measurements. In the appendix will be given some examples of the necessary figures, the setting up of the balance in the most suitable form, and the basis on which the heat exchange figure is calculated. The computed values show a dependency of the heat exchange figure on the temperatures of the material being burned, so that it was possible to combine the values over the corresponding clinkering temperatures in a curve, and to use this curve (Fig. 5) as a basis for precalculations. The calculation gave the following values for plotting the curve :

Clinkering temperature (deg. C.)	1525	1450	1420	1410	1410	1400
Heat exchange factor (kcal. per square metre per hour per deg. C.)	36·1	33·6	33·2	33·1	33·1	33·0

The feed temperature of the raw material varied between 27·7 and 35 deg. C. with an average of 30 deg. C.

With the use of the Lepol kiln or the Miag calcinator the temperatures of the raw material at the inlet of the kiln are considerably higher. To determine the influence of these higher temperatures on the heat exchange factor the course of the values for m was calculated in sections over the length of the kiln from Professor Nacken's temperature measurement on the rotary kiln (Fig. 6).

Starting-points were the values of the temperatures of the material burned (curve 1) measured by Professor Nacken and of the flue-gas temperature (curve 2) and also (curve 4) on the driving out of the carbonic acid from the raw meal.

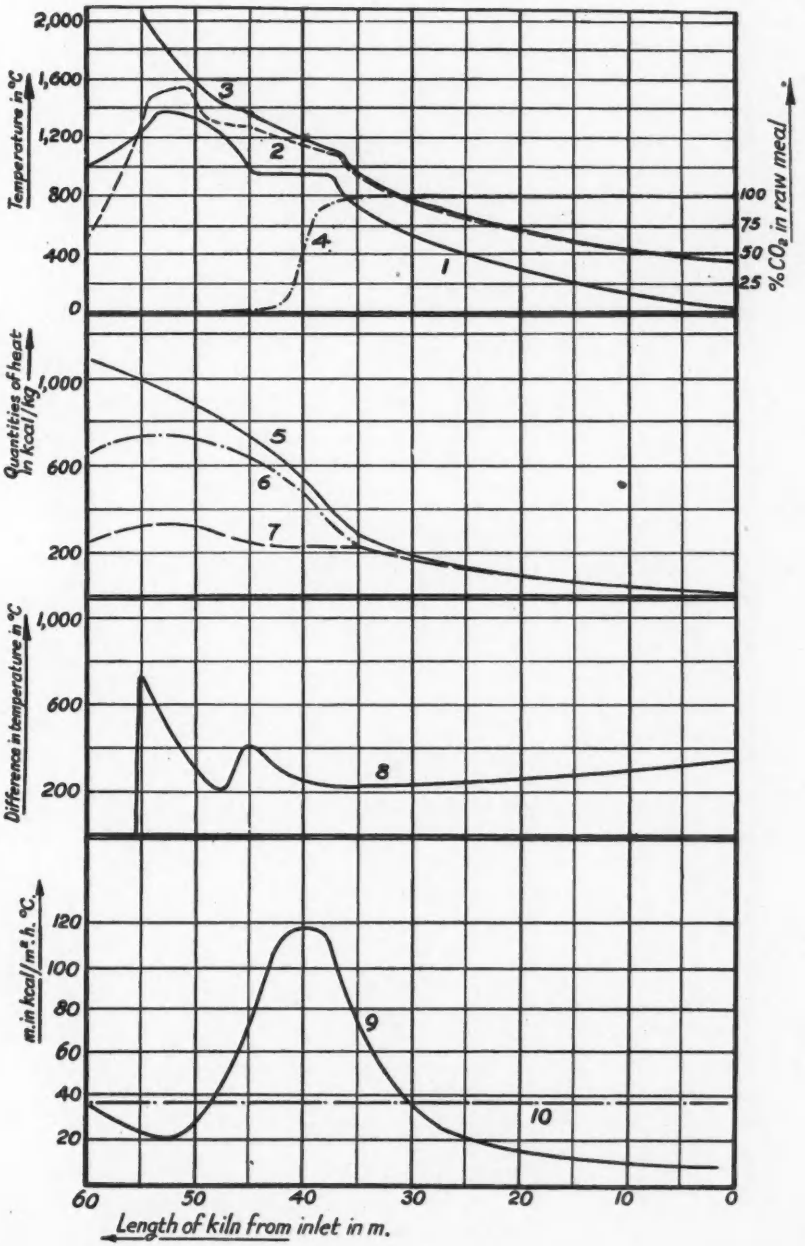
Temperature in °C
2,000
1,600
1,200
800
400
0
3
2
4
1
100
75
50
25
% CO_2 in raw meal
Quantities of heat in kcal/kg
1,000
600
200
5
6
7
Difference in temperature in °C
1,000
600
200
8
m. in kcal/m². h. °C.
120
100
80
60
40
20
9
10
60
50
40
30
20
10
0
Length of kiln from inlet in m.

Fig. 6.

This curve deviates at first from the value measured by Timm and Nacken on a kiln after stoppage. Tests made in the laboratory on the connection between the driving out the carbonic acid and the temperature of the material burned gave rise to the conjecture that the contents of neutralised raw meal found in the inlet of the kiln are attributable to the formation and deposition of flue dust. Therefore only the values at the end of the driving out of the carbonic acid were used from previous measurements, and the beginning of the curve corrected according to the finding of laboratory examinations. With the help of curve 1 the shell losses of the rotary kiln were determined section by section, and then the whole heat passing over was ascertained (curve 5). Curves 6 and 7 show the subdivision of this heat in perceptible heat of the material burned, chemical heat, and shell losses. From this curve 3 could be reconstructed, giving the theoretical flue-gas temperatures, and with its help curve 8 of the temperature differences and curve 9 of the true values of M were obtained.

On account of various assumptions, and also because of the number of sections finally used in the curve, naturally agreement was obtained in the order of size of the figure with the computed average values. It proved, however, that the values at the feed end of the kiln can be considered as relatively correct, and that the variation of the mean values may be predetermined from the knowledge of the mean ordinates and the true values of M from this curve at temperatures up to 300 deg. C.

The installation of a calcinator or of a Lepol grate would correspond to the cutting off of the kiln at the abscissa (a) where the measured temperature of the material burned and the feed temperature of the granulated material correspond. The area of curve $F = {}_0\int^e M dl = m.l.$ is therefore smaller by the portion $f = {}_0\int^a M.dl$, and the new value for m is therefore obtained from the calculation

$$m' = \frac{m.l - {}_0\int^a M.dl}{l - a} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9)$$

Computations of heat consumption made on the basis of the values found in this manner for operation with the Miag calcinator agreed well in all details with test measurements made independently, so that this extension of the heat exchange figures found by measurement seems permissible.

The value of the mean heat exchange figure being fixed by this means, the curve for flue-gas heat can be computed, and from the intersection of the line of heat required and the line of flue-gas heat the temperature of the waste gas can be determined. The size of the ordinate of the point of intersection, corresponding to the definition of the line of heat required, indicates simultaneously the amount of the shell losses of the rotary tube at the computed waste-gas temperature.

(To be continued.)

Components and Systems Having a Possible Bearing on Portland Cement Clinker Constitution.

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

A COMPOUND is said to melt congruently if at the melting point the solid and liquid in equilibrium have the same composition. On the other hand a compound melts incongruently when at the melting point the liquid and solid in equilibrium have different compositions.

Compounds that melt congruently at temperatures below 1,700 deg. C. are easily prepared. A mixture of the finely ground pure components can be melted in a platinum vessel and maintained in the liquid condition long enough for diffusion to establish homogeneity. Compounds that melt above 1,700 deg. C. are not so easy to make because of the difficulty of getting crucibles to withstand these temperatures without reacting with the melt. Compounds subject to dissociation at or below the melting point are difficult to prepare. The processes of heating for a long time to a temperature at which no dissociation occurs, cooling, and then grinding, have to be repeated several times as a general rule.

Calcium Oxide and Hydroxide, CaO and $Ca(OH)_2$ [1 to 7]

Calcium oxide has only one crystalline form at high temperatures. It forms directly from highly basic silicate melts or from fused calcium nitrate. In a basic silicate melt the free lime appears usually in fine isotropic colourless grains, generally rounded in outline. The grains are easily recognisable even when only a few thousandths of a millimetre in diameter. Well-developed crystals are only obtained from relatively large melts of pure calcium oxide ; the crystals belong to the isometric system, being transparent unmodified cubes, the cleavage being perfect (100). Refractive index = 1.83. Density = 3.316 (25 deg. C.). Melting point, 2,570 deg. C.[7]

According to Sosman[6] this form of calcium oxide inverts to another crystalline variety at 420 deg. C., but this has not been thoroughly studied. The rate of hydration of calcium oxide varies according to the temperatures to which it has been exposed and the fineness to which it has been ground ; it increases the finer the material and the lower the temperature to which it has been heated. This being so, supersaturated solutions are quickly formed and calcium hydroxide is precipitated in the amorphous condition. When calcium hydroxide hydrates very slowly (coarse hard-burnt material) a saturated solution is only slowly formed and crystals of calcium hydroxide are deposited. These crystals are much more inactive chemically than the amorphous variety. White's reagent, which attacks the amorphous form almost instantly, reacts much more slowly with the crystals. Calcium hydroxide crystals[2 3 4] are short flaky hexagonal plates and prisms. They are formed by (1) hydration of coarse hard-burnt CaO ; (2) slow evaporation of calcium hydroxide solution ; (3) electrolysis of calcium chloride solution ; (4) Johnston diffusion method.[5] The specific gravity =2.239.[5] Refractive indices (sodium light) are $\omega = 1.574 \pm 0.003$, and $\epsilon = 1.545 \pm 0.003$.

The optical character is negative. Birefraction = 0.029. The crystals closely resemble hydrated tricalcium aluminate crystals ($3CaO.Al_2O_3.xH_2O$) but the aluminate crystals are invariably larger and have a higher refractive index.

Silica (SiO_2)[6, 9 to 17]

There are three principal forms of silica, namely, quartz, tridymite, and cristobalite. Silica responds very slowly to temperature changes as affecting melting point and transition from one form to another. Each principal form, however, has one or two inversion points which respond promptly to temperature changes. Fused silica is stable only above 1,625 deg. C. Table I gives the stability of the different crystalline modifications of silica (reference No. 9 unless otherwise stated).

TABLE I.

Inversion.	Temperature. Deg. C.	Remarks.
α-quartz $\longleftrightarrow$ β-quartz	573.3 (reference 13)	Rapid and reversible. Latent heat of inversion = 3.1 cal. per gram. (Reference No. 14.)
β-quartz $\longleftrightarrow$ β_2-tridymite.	870 $\pm$10	Very sluggish; reversible.
β_2-tridymite $\longleftrightarrow$ β-cristobalite.	1,470 $\pm$10	Very sluggish; reversible.
α-tridymite $\longleftrightarrow$ β_1-tridymite.	117	Rapid; reversible.
β_1-tridymite $\longleftrightarrow$ β_2-tridymite.	163	Rapid; reversible.
α-cristobalite $\longleftrightarrow$ β-cristobalite.	220–275	Rapid; reversible. Temperature depends on previous heat treatment.

The forms which exist at low temperatures are α-quartz, α-tridymite, α-cristobalite, and chalcedony. According to Ferguson and Merwin,[10] cristobalite melts at 1,710 deg. C. $\pm$ 10 deg. C. Metastable tridymite melts at 1,670 deg. C. $\pm$ 10 deg. C., and metastable quartz at 1,470 deg. C.

HYDRATES OF SILICA.—Silica can exist in the form of a colloidal solution, or as gelatinous hydrated silica, or as insoluble silica. Thus the action of acids on solutions of sodium or potassium silicates produces a gelatinous hydrated silica which is appreciably soluble in water to form a colloidal solution. It is soluble also in alkali and sodium carbonate to form salts. When heated to 100 deg. C. 13 per cent. of the water remains and the silica is then insoluble. On heating to 500 deg. C. all water is lost.

The question arises as to whether there are definite silicic acids (i.e., definite hydrates of silica) corresponding to the various silicates. When silicon tetrachloride is decomposed by water, a hydrated gelatinous form of silica is precipitated. This is often assumed to be orthosilicic acid, $Si(OH)_4$, or $SiO_2.2H_2O$;

it has this composition when washed rapidly with benzene and ether and dried between filter paper at atmospheric temperature. Gelatinous hydrated silica precipitated by the addition of mineral acids to solutions of sodium or potassium silicates, when dried in the air, retains about 16 per cent. of water corresponding roughly to the formula

$$SiO(OH)_2 \text{ or } SiO_2.H_2O, \text{ metasilicic acid.}$$

The relations between the ortho- and meta-acids and the anhydride would be

$$Si(OH)_4 \xrightarrow{-H_2O} SiO(OH)_2 \xrightarrow{-H_2O} SiO_2$$

or

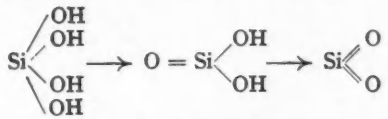

TABLE II.

PROPERTIES OF THE FORMS OF SILICA.

Form.	Crystal system.	Crystal habit.	Refractive indices.	Optic character.	Optic axial angle.
α-quartz	Trapezohedral.	—	$\alpha = 1.544$ $\gamma = 1.553$	Positive.	Uni-axial.
β-quartz	Trapezohedral. Hexagonal. Hemihedral.	Pyramidal.	—	,,	,,
α-tridymite .... Density = 2.27.	Orthorhombic.	Pseudo-hexagonal plates (thin).	$\alpha = 1.469$ $\gamma = 1.473$	,,	Large.
β-tridymite	Hexagonal.	Hexagonal plates.	—	,,	Uni-axial.
α-cristobalite ..	Probably tetragonal.	Cryptocryst aggregates.	$\alpha = 1.484$ $\gamma = 1.487$	—	—
β-cristobalite .. Density = 2.32.	Isometric.	—	—	—	—

It cannot, however, be considered as proved that two definite compounds corresponding with the formulæ $SiO_2.H_2O$ and $SiO_2.2H_2O$ exist. Doubt has often been thrown on the existence of definite hydrates of silica. There is no doubt, however, of the existence of the ethyl esters of ortho- and meta-silicic acids; the molecular weights of these bodies prove their formula to be

$$Si(OC_2H_5)_4 \text{ and } SiO(OC_2H_5)_2,$$

i.e., they must be derived from acids of the type

$$Si(OH)_4 \text{ and } SiO(OH)_2$$

According to Schwarz,[15] silica can form the hydrates $SiO_2.H_2O$ and $2SiO_2.H_2O$ which are hexameric. They are obtained by the decomposition of sodium silicates with 80 per cent. sulphuric acid, as well as by the hydrolysis of solutions of the alkali salts. In these solutions the ions SiO_3'' and Si_2O_5'' are in an equilibrium which is displaced in favour of Si_2O_5'' with increasing hydrogen ion

concentration. In silica gels Okazawa[17] claims to have demonstrated the presence of the hydrates $SiO_2.H_2O$ and $SiO_2.2H_2O$. According to Biltz and Rahlfs[16] the formula of disilicic hydrate is $6SiO_2.3H_2O$.

Alumina and Hydrated Alumina

Hydrated alumina may be prepared by double decomposition of aluminium chloride and ammonium hydroxide at room temperature. According to Hansen and Brownmiller[18] the precipitate after drying to constant weight at 110 deg. C. has the formula $Al_2(OH)_6$ or $Al_2O_3.3H_2O$. According to Rooksby[19] the product is a mixture of $Al_2O_3.H_2O$ and $Al_2O_3.3H_2O$.

When hydrated alumina is precipitated from an aluminate solution its formula is $Al_2O_3.3H_2O$. Although it has the same chemical composition as the mineral gibbsite it has a different X-ray diffraction pattern. On heating for 40 to 50 hours at 200–215 deg. C. $Al_2O_3.3H_2O$ loses two molecules of water and becomes converted to $Al_2O_3.H_2O$, which formula corresponds to that of the mineral diaspore. According to Rooksby[19] its X-ray diffraction pattern is different from that of diaspore and is identical with that of many bauxites. According to Brownmiller and Hansen[18] it gives no X-ray diffraction pattern indicating that it is amorphous. Examined microscopically it is found to be very fine grained; the refractive index of the aggregates is 1.565 ± 0.003. $Al_2O_3.3H_2O$ ignited at temperatures between 400 and 800 deg. C. yields anhydrous amorphous alumina, Al_2O_3; the refractive index of the aggregates equals 1.65 to 1.69. $Al_2O_3.3H_2O$ heated for six hours at 900 to 950 deg. C. yields a crystalline anhydrous variety of alumina. The product is isotropic with refractive index of 1.696 ± 0.003 and a density of 3.47. This is probably the same material reported by Ullrich[20] as γ-alumina. The X-ray diffraction pattern does not correspond to that of the β-alumina described by Rankin and Merwin.[21] $Al_2O_3.3H_2O$ heated for one hour at 1,200 deg. C. yields the crystalline anhydrous modification of alumina known as artificial corundum. It has the following properties: Grains crystallised from a melt of pure alumina rarely show crystal outline; they are rounded in outline and less than 0.05 mm. in diameter. Minute air cavities are abundant and characteristic. Its melting point is 2,050 deg. C.[7]; hardness, 9; crystal system, hexagonal; refractive index (sodium light), $\alpha = 1.760$, $\gamma = 1.768$; optical character, negative; optic axial angle, uniaxial; birefringence, fairly weak (about 0.009). From mixtures it usually crystallises in thin and sharply defined hexagonal plates. Optically the properties of artificial corundum agree well with those of the natural mineral.

Oxides of Iron

There are three well-known oxides of iron, namely, ferrous oxide (FeO), ferric oxide (Fe_2O_3), and ferroso-ferric oxide (Fe_3O_4). Ferrous oxide is said to melt at 1,355 deg. C. (approximately)[22] and is of a decidedly basic character. Ferric oxide is amphoteric and its melting point is not accurately known; various figures about 1,560 deg. C. have been put forward. It has a sharp reversible inversion point at 678 deg. C. accompanied by heat absorption and a drop in

magnetic susceptibility; Fe_3O_4 is said to have similar magnetic inversion at 530 deg. C. Fe_3O_4 is strongly magnetic and is said to melt between 1,540 and 1,580 deg. C.

When ferric oxide is heated, dissociation commences at 1,100 deg. C.[23 24] according to the equation

$$6Fe_2O_3 \longleftrightarrow 4Fe_3O_4 + O_2$$

Sosman and Hostetter[24] have shown that the extent of the dissociation increases with rise of temperature and time of heating. They point out that artificial oxides of iron at 1,100 to 1,200 deg. C. consist of solid solutions of Fe_3O_4 in Fe_2O_3.

THE SYSTEM MgO-CaO.[65].—The temperature range of this system is too high for satisfactory investigation, but it is considered to be an eutectic series with no compounds formed and little of any solid solution.

THE SYSTEM $MgO-SiO_2$.[66].—Besides the components, two compounds occur in this system: (1) clinoenstatite, $MgO.SiO_2$—when pure this body dissociates when melting begins; and (2) forsterite, $2MgO.SiO_2$.

THE SYSTEM $MgO-Al_2O_3$ AND THE SYSTEM $MgO-Fe_2O_3$.[25 26].—There is only one compound of magnesia and alumina, namely, spinel ($MgO.Al_2O_3$) and it may be prepared by heating an intimate mixture of magnesia and alumina several times at 1,500 deg. C., the preparation being reground between the heatings. It is insoluble in acids and melts at 2,135 deg. C. $\pm$ 20 deg. C. The refractive index is 1.723 ± 0.003.

$MgO.Fe_2O_3$ may be prepared by heating an intimate mixture of MgO and Fe_2O_3 at 1,450 deg. C. It consists of small isotropic grains with refractive index 2.34 ± 0.01 (lithium light). $MgO.Al_2O_3$ and $MgO.Fe_2O_3$ appear to form solid solutions, at least to a limited extent.

THE SYSTEM $Al_2O_3-Fe_2O_3$.—Forestier and Chaudron[27] report that no compounds are formed, but that ferric oxide takes up about 12 per cent. alumina in solid solution. This was determined by a thermal dilatometric method upon mixtures of precipitated oxides which had been previously heated to 900 deg. C. Hansen and Brownmiller[26] studied the system by precipitating the components together from solutions of their chlorides. The mixed precipitate was heated for one hour at 1,200 deg. C. and studied by the X-ray diffraction method.

Ferric oxide was found to take up to 10 to 15 per cent. alumina in solid solution. Alumina takes up a very little ferric oxide in solid solution.

THE SYSTEM $Al_2O_3-SiO_2$.[28].—Only one compound, $Al_2O_3.SiO_2$, is stable in contact with the melt, the optical properties agreeing quite well with those of the mineral sillimanite. The other two minerals, cyanite and andalusite, which have the same composition, slowly change into sillimanite at temperatures above 1,300 deg. C.

Artificial sillimanite melts at $1,816 \pm 10$ deg. C. and forms eutectic mixtures both with alumina and with silica. It crystallises from a melt as fine grained, fibrous lath shaped individuals. Its crystal system is orthorhombic; refractive indices, $\alpha = 1.638$, $\beta = 1.642$, $\gamma = 1.653$ (sodium light); optical character,

positive; optic axial angle, small; birefringence, medium ($\gamma - \alpha$ about 0.014). The refractive indices are slightly lower than in the natural mineral.

THE SYSTEMS FeO-SiO_2 and FeO-Fe_2O_3-SiO_2.—The system FeO-SiO_2 has been investigated by Herty and Fitterer.[29] Fayalite, $2FeO.SiO_2$, melts at 1,335 deg. C. The fayalite-FeO eutectic contains 22 per cent. silica, and melts at 1,240 deg. C. The fayalite-tridymite eutectic contains 35 per cent. silica and melts at 1,260 deg. C.

In a study of liquid immiscibility in the system FeO-Fe_2O_3-SiO_2, Greig[30] was able to extrapolate to the binary system FeO-SiO_2 with fair certainty. The system separates into two immiscible layers, one having the composition 3% FeO + 97% SiO_2 by weight; the other 42% FeO + 58% SiO_2, and the temperature at which this occurs is 1,690 deg. C. It was found that the amount of alumina necessary to cause a single liquid to result from the melting of mixtures in the quaternary system FeO-Fe_2O_3-Al_2O_3-SiO_2 varies with the silica content and the ferrous-ferric ratio.

Percy[31] mentions that silica added to mixtures of calcium oxide and ferric oxide reduces the latter at high temperatures with the formation of FeO-SiO_2 compounds. These can be oxidised again at lower temperatures yielding CaO-Fe_2O_3 compounds.

(To be continued.)

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Studies on the Celite Part of Portland Cement.

By SHOICHIRO NAGAI and GENTARO SAWAYAMA.

THE following is an abstract of a report by Messrs. Shoichiro Nagai and Gentaro Sawayama of the Institute of Silicate Industry of Tokyo Imperial University.

The celite part of Portland Cement is generally believed to be $4CaO.Al_2O_3.Fe_2O_3$ (A. E. Tornebohm, Die Petrographie des Portlandzements, Stockholm, 1897; *Tonindustrie-Zeitung*, 1897, 31, 1148, 1157). But Jaenecke (*Zementprotokoll*, 1928—1929, 51, 28) reported that the composition of the celite part contains $6CaO.Al_2O_3.2Fe_2O_3$, which is richer in ferric oxide than $4CaO.Al_2O_3.Fe_2O_3$. Recently, Spohn (Dissertation der Technischen Hochschüle zu Berlin, 1932) pointed out that $4CaO.Al_2O_3.Fe_2O_3$ can be synthesised when the cement contains alumina and ferric oxide in equal quantities. Haegermann (Vortrag der Generalversammlung des Vereins Deutscher Portlandzement-Fabrikanten, Berlin, 1933) stated that the conglomerate of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ is produced by separating calcium aluminate when the mixture containing 3 to 4 per cent. excess lime of $4CaO.Al_2O_3.Fe_2O_3$ is treated at melting temperature. On the other hand, Solacolu (*Zement*, 1932, 21, 301), reported that $4CaO.Al_2O_3.Fe_2O_3$ is not decomposed to calcium aluminate and conglomerate of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ by the excess lime, as reported by Haegermann. The present authors studied the combinations between CaO, Al_2O_3 and Fe_2O_3 of the celite part and the results are briefly summarised as follows.

(1) Results of heating of mixture ($4CaO.Al_2O_3.Fe_2O_3$) at 1250 deg. C. The mixture was heated at 1250 deg. C. for several hours. The products were analysed for free lime, insoluble residue or uncombined alumina, and combined lime, alumina and ferric oxide. The results are given in Table I.

TABLE I.

Heating Time (Hours).	Free CaO (Per cent.).	Insoluble Residue (Per cent.).	Combined		
			CaO (Per cent.).	Al_2O_3 (Per cent.).	Fe_2O_3 (Per cent.).
6	1.25	0.35	44.91	20.70	32.79
12	0.21	0.35	45.95	20.70	32.79
18	0	0	46.16	20.70	32.79

The mixture combines very easily even at a low heating temperature of 1250 deg. C. Four mol. of lime combine with 1 mol. of Al_2O_3 and 1 mol. of Fe_2O_3. When the lime content is increased to 5 mol. the combination of lime with alumina and ferric oxide is very difficult.

(2) Results of heating of mixture ($5CaO.Al_2O_3.Fe_2O_3$).—The mixture was heated at 1250, 1320, 1370 and 1400 deg. C., and the heated products were treated as already described. The results are shown in Table II.

In the table the sign 6 (+42) hours at 1320 deg. C. means that the sample, which had been heated seven times for periods of six hours each at 1250 deg. C. until

TABLE II.

Heating Temperature (Deg. C.).	Heating Time (Hours).	Free CaO (Per cent.).	Insoluble Residue (Per cent.).	Combined		
				CaO. (Per cent.).	Al_2O_3. (Per cent.).	Fe_2O_3. (Per cent.).
1250	6	12.14	0	39.59	18.71	29.56
1250	12	12.03	0	39.70	18.71	29.56
1250	24	6.34	0	45.39	18.71	29.56
1250	42	5.92	0	45.81	18.71	29.56
1320	6 (+42)	5.87	0	45.86	18.71	29.56
1320	12 (+42)	5.95	0	45.78	18.71	29.56
1400	6 (+66)	7.90	0	43.83	18.71	29.56
1400	30 (+66)	9.10	0	42.65	18.71	29.56

there was no sign of reaction, was heated for a further six hours at 1320 deg. C. The other signs indicate similar heating conditions. As is seen from the table, the heated product contained 5.95 per cent. of free lime and the reaction proceeded no further by continued heating at a temperature of 1250 to 1370 deg. C., but by heating at a higher temperature of 1400 deg. C. the sample separates out more free lime (9.10 per cent.). This shows that the mixture $5CaO.Al_2O_3.Fe_2O_3$ produces several different compounds under different heating conditions.

By heating at 1250 to 1370 deg. C. the mixture $5CaO.Al_2O_3.Fe_2O_3$ changes to $6CaO.Al_2O_3.2Fe_2O_3$ and $3CaO.Al_2O_3$, which corresponds to the separation of 5.14 per cent. free lime. If $6CaO.Al_2O_3.2Fe_2O_3$ is assumed to be a conglomerate between $2\times 2CaO.Fe_2O_3$ and the eutectic mixture of CaO 47 per cent. and Al_2O_3 53 per cent. from $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$, the free lime will be 6.14 per cent., which corresponds to the minimum amount of free lime (5.9 to 6.0 per cent.) in Table II. When the mixture was heated at 1400 deg. C., free lime increased gradually to 9.1 per cent.

(3) Results of heating the mixture ($5CaO.Al_2O_3.Fe_2O_3$).—The mixture was directly heated at 1400 deg. C. and then repeated at 1420 deg. C. The results are shown in Table III, and it is clear that the amount of free lime coincides with that obtained in Table II by repeated heating at 1400 deg. C., but this amount decreased suddenly to 4.9 to 5.0 per cent. by heating at 1420 deg. C.

TABLE III.

Heating Temperature (Deg. C.).	Heating Time (Hours).	Free CaO (Per cent.).	Insoluble Residue (Per cent.).	Combined		
				CaO (Per cent.).	Al_2O_3 (Per cent.).	Fe_2O_3 (Per cent.).
1400	6	7.10	0	44.63	18.71	29.56
1400	12	9.05	0	42.68	18.71	29.56
1400	18	9.01	0	42.72	18.71	29.56
1420	6(+42)	4.96	0	46.77	18.71	29.56
1420	12 (+42)	4.91	0	46.82	18.71	29.56

The 9.1 per cent. of free lime in the second and third lines of Table III is less than the 10.3 per cent. which can be obtained by calculation on the assumption that these heated products are composed of the sintered mixture of $2CaO.Fe_2O_3$ and the eutectic between $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ (CaO 47 per cent. and Al_2O_3 53 per cent.). But this difference of about 1 per cent. of free lime is due to

the difficulty of determining free lime in the strongly sintered or melted product, and is the defect of Lerch and Bogue's method. The last two experiments were a continuation of the experiment referred to in line 4 of Table II, and the decrease of the amount of free lime to 4.9 to 5 per cent. is due to complete melting of the heated products at 1420 deg. C.

(4) Results of heating the mixture ($3CaO.Al_2O_3$ and $2CaO.Fe_2O_3$) at 1320 deg. C.—Tricalcium aluminate $3CaO.Al_2O_3$ and dicalcium ferrite $2CaO.Fe_2O_3$ were separately synthesised and mixed in equal proportions, equal to $5CaO.Al_2O_3.Fe_2O_3$ in three components. This mixture was heated and analysed under the same conditions, and the results are given in Table IV.

TABLE IV.

Heating Temperature (Deg. C.).	Heating Time (Hours).	Free CaO (Per cent.).	Insoluble Residue (Per cent.).	Combined		
				CaO (Per cent.).	Al_2O_3 (Per cent.).	Fe_2O_3 (Per cent.).
1320	5	1.45	0	50.78	29.52	19.15
1320	10	2.14	0	49.09	29.52	19.15
1320	28	4.12	0	47.11	29.52	19.15
1320	50	5.30	0	45.93	29.52	19.15

The sample gradually set lime free up to the amount of 5.3 per cent. by heating at 1320 deg. C. for 40 to 50 hours. This amount of free lime compares well with the calculated amount (5.14 per cent.) on the assumption that the mixture changes to $6CaO.Al_2O_3.Fe_2O_3$, $3CaO.Al_2O_3$ and CaO, by heating at relatively lower temperature (1250 to 1320 deg. C.). Thus, by heating the mixture of synthesised $3CaO.Al_2O_3$ and $2CaO.Fe_2O_3$ at relatively low temperature some part of $3CaO.Al_2O_3$ reacting with $2CaO.Fe_2O_3$ changes to $6CaO.Al_2O_3.2Fe_2O_3$ and CaO, the free lime amounting to 5.1 per cent. theoretically, or 5.3 per cent. experimentally as shown in the table.

The result of heating the mixture $5CaO.Al_2O_3.Fe_2O_3$ or $3CaO.Al_2O_3+2CaO.Fe_2O_3$ at a relatively low temperature (1250 to 1320 deg. C.) coincides well with Haegermann's report. The result of heating at relatively high temperature (1400 to 1420 deg. C.) coincides well with Solacolu's results, so that the decomposition of the celite part $4CaO.Al_2O_3.Fe_2O_3$ by excess lime depends mainly upon the heating temperatures.

Action of Sea Water in Slurry on the Clinker-Brick Lining of a Rotary Kiln. By K. Krassowsky (*Tonindustrie-Zeitung*, No. 33, 1934).—Clinker bricks burnt through in five days when sea water was used in the slurry, instead of lasting twenty to thirty-five days as is the case when fresh water is used. The cause is obscure, as an analysis of the bricks after four days' use did not show an unusual amount of alkali.

Effect of Trass-cement on Large Masses of Concrete.

By Dr. K. BIEHL.

EXTENSIVE investigations carried out in the United States on structures containing large masses of concrete, such as dams, walls, etc., as reported on by W. H. Rabe[1], have resulted in information which is of interest not only to the contractor but also to the cement manufacturer. Cracks which have appeared in dams and other structures where large masses of concrete are used supplied the reason for these investigations.

Available information suggests three reasons for the appearance of cracks, namely static and physical causes, and thermo-chemical reactions. Cracks due to static causes can be traced to the influence of external loads, movement of bearing points, or resilience of subsoil. Cracks due to physical causes are the results of wide variations in external temperatures as well as opportunities for the transfer of heat from the concrete. Transfer of heat from concrete, which is of particular importance in this direction, depends on conditions which vary according to the situation and size of the structure, the kind of aggregate used, the speed of placing the concrete, climate, etc.

Cracks from thermo-chemical reactions are mainly caused by the heat of hydration of cements, which brings the concrete to a high temperature. This is dependent on the proportion of cement to aggregate, and on the brand and type of cement used. The cracks are a result of shrinkage when the mass of concrete cools. The investigations further show that the influence of outside temperature is less important than the heat of hydration of the cement, that heat conductivity varies little if at all with variations of the mixture of concrete, and that opportunities for the transfer of heat may vary considerably with different structures.

It is therefore shown that while most of the causes of cracks are varying external conditions and influences which may be eliminated by special care, the heat of hydration of cement is a factor which can only be regulated under special conditions. Experiments seem to point to the relationship of the heat of hydration to such factors as chemical composition and physical characteristics of cements and it should be possible also to minimise or avoid these sources of cracks in concrete.

Carlson ascribes high heat of hydration to a high percentage of $3CaO\ SiO_2$. He explains this by the fact that cements have materially changed in their mineralogical structure during the last decade, mainly in the direction of high lime content. This causes increase of tricalcium-silicate whilst reducing dicalcium-silicate. Cements high in ferric oxide and alumina are said to show less shrinkage. Further, the finer grinding of cements is stated to account for increased shrinkage and intensified reactions with higher heat of hydration.

United States investigations show that types of cement with intensive reaction and consequently high heat of hydration are unsuitable for structures

containing large masses of concrete. Carlson gives the following requirements of a cement to be used for structures with large masses of concrete: (1) low variations of temperature during hydration and cooling; (2) sufficiently rapid hardening to allow economical use of shuttering; (3) sufficiently high final strength; (4) low changes of volume and elimination of cracks as far as possible; (5) durability; (6) watertightness; (7) no important difference in price compared with standard cements and no special difficulties in mixing or placing.

Generally speaking there are two ways along which these requirements can be met.

For instance, a cement might be produced which, as a result of its chemical composition, would evolve very little heat; Carlson suggests a coarsely-ground cement with a minimum of tricalcium-silicate, that is, a complete change in the chemical composition of cements. There is no doubt that the properties of cements will be affected by this. The demand for high strengths produced finer grinding and increase of lime content with resultant increase of tricalcium-silicate; this in turn increased the intensity of reactions and the heat of hydration. The only method of reducing the heat of hydration of certain present-day cements seems to be the manufacture of cements with a low lime content in order to reduce excessive formation of tricalcium-silicate. With ordinary cements this will result in a reduction of strength, which from the consumers' point of view is undesirable except in very few cases. It is, however, possible for the manufacturer to meet the demand for a reduction in the heat of hydration by making special cements for special purposes.

Another possibility of reducing heat of hydration involves the admixture to the concrete of materials which reduce the heat of hydration. Suitable hydraulic materials which participate in the setting and hardening under the influence of lime or derivates of lime are available for this purpose, such as trass. Cements containing percentages of trass have been on the market for some years now, the mixtures containing 70 per cent. of Portland cement clinker and 30 per cent. of trass, or 50 per cent. of Portland cement clinker and 50 per cent. of trass. Alternatively the consumer can add trass to cement in the desired proportions on the building site. In this case the cement and trass should be mixed dry before adding the aggregate and water. Experiments show a considerable reduction in the heat of hydration when part of the cement is replaced by trass. Tests have shown that the temperature of high-strength Portland cement reaches 24.8 deg. C. 22 hours after it has been placed, whereas the maximum temperature of the same cement diluted with 30 per cent. of trass reaches a maximum temperature of 20.3 deg. C. Similar tests on ordinary Portland cement give a maximum temperature of 22.9 deg. C. at 21 hours, whereas the same cement diluted with 30 per cent. of trass reaches a maximum temperature of 18.8 deg. C. after the same period.

The demand for rapid hardening cement can also be satisfied by trass-cements. Such cements harden as quickly as standard Portland cements, while the 70 : 30

mixture is supplied in a high-strength quality. Trass-cement concrete has a good final strength, particularly tensile strength, and elasticity of the concrete is considerably improved as has been shown by Ostendorf[2], Guttmann[3], Graf[4], and others.

Volume changes of structures in water when made with trass-cement can hardly take place[2]. The addition of trass considerably reduces the heat of hydration. Low permeability is ensured because, under the influence of the lime during the setting of cement, the trass swells and fills the pores of the concrete[5]. Concrete made with trass-cement is particularly plastic and is eminently suitable for casting[5], and its resistance to chemical influences is increased.

Trass-cements have lime contents as follows:

70 cement : 30 trass, lime content 47 ± 2 per cent.
50 cement : 50 trass, lime content 35 ± 2 per cent.

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[1] W. H. Rabe.—Changes in volume of concrete in dams under the influence of temperature, heat of hydration, and shrinkage. *Zement*, 1933, p. 278. Investigations on large masses of concrete and special cements for the Hoover-dam. *Zement*, 1933, p. 388.
[2] K. Ostendorf.—Suitable concrete mixtures for work in water, Berlin, 1927. Importance of trass-Portland-cement, Amsterdam, 1931.
[3] A. Guttmann.—Trass Portland cements, *Tonind. Ztg.*, 1932, 4, 6, 7.
[4] O. Graf.—German Committee for Reinforced Concrete.
[5] Vetter & Rissel.—Choice of materials for concrete structures. Berlin, 1933.

The Zeolitic Nature of Trass. By K. Biehl and W. Wittekindt (*Tonindustrie-Zeitung*, Nos. 41 and 42, 1934).—Nettaler tuff showed distinct zeolitic properties. When shaken with calcium nitrate alkalis and with sodium choride lime it went into solution. Rhine, Ettringer, Brohler Berg, Rhön, Rome, and Dej trasses showed the same effects. In general the absorption of lime rose with increase in fineness of the trass. The natural zeolites showed a lower capacity for base exchange than most of these trasses.

In No. 49, 1934, of the same journal, A. Steopoe deals with the same subject. He states that the base exchange capacity of Rumanian trasses from Slanic and Dej could be considerably altered by previous treatment. HCl reduced the activity, while NaOH more than doubled it. The base exchange capacity depends largely on the amount of active alkali present in the trass.

Standard Sand. By F. Richner (*Tonindustrie-Zeitung*, No. 46, 1934).—Two cements (*A* and *B*) which gave the same strength figures in the standard tests gave quite different relative figures in practice with building sand. Cement *B*, gave a much higher strength than *A*, and also contained more SO_3. When the SO_3 in *A* was made the same as in *B* the two cements gave the same results. Further tests with other sands showed that the relative strength figures varied considerably. This shows that the standard test does not always give a relative idea of how cements will behave in practice.

"Morbelli" Cement.

A REPORT is given in " T.I.Z." (97/1933) on a new material similar to asbestos cement, which is said to allow considerable saving of cement and to possess chemical and physical qualities making it superior to asbestos cement. The inventor—Dr. Morbelli of Milan—started with the object of fixing as early as possible the hydrate of lime liberated on hydration of cement and to improve the watertightness and resistance of concrete to chemical attack.

The use of pozzolana was not entirely successful, because of the time taken to bind the lime and the hydrate of lime. Dr. Morbelli makes use of a fundamental law of chemistry—the speeding up of reactions when pressure and temperature are increased—to secure the binding of lime by silica. This principle has been in commercial use for some time in the manufacture of sand-lime bricks.

The Morbelli process consists in the grinding together of Portland cement with such quantities of silica as will allow complete combination of the liberated hydrate of lime followed by the placing of the set mixture for some hours in an autoclave under a steam pressure of about 8 atmospheres. Tests made by the Soc. An. Eternit Genova have shown that the strength of this product is higher than that of high quality asbestos cement, although 75 per cent. of the usual cement content used had been replaced by ground quartz. Resistance to abrasion was improved by about 20 times. The resistance to acids is also excellent. Tests made by Dr. Kühl show that Morbelli-cement loses only about one-third of the weight lost by ordinary asbestos cement when placed in diluted hydrochloric acid for four weeks. Table I gives the results of tests on samples stored in acids.

TABLE I

Stored in diluted acid.		Tensile strength in kg. per sq. cm. after storage for			Remarks.
		1 Week.	2 Weeks.	4 Weeks.	
Hydrochloric acid ..	Asbestos-cement	50	0	0	Material crumbled and swollen.
Do.	Morbelli asbestos cement	130	150	180	No loss of shape.
Nitric acid	Asbestos cement	0	0	0	Material crumbled and swollen.
Do.	Morbelli asbestos cement	170	170	175	No loss of shape.

Microscopical examination showed that the larger part of the quartz shows considerable changes of structure, so that it seems incorrect to ascribe the results to insolubility of the silica which has replaced three-quarters of the cement. A drop of concentrated hydrochloric acid on Morbelli cement causes no trace of the silica-gel formation to be observed on ordinary asbestos cement. It therefore seems that most of the quartz is used in the formation of calcium hydro-

silicate; analysis shows a ratio of 1 CaO : 5 SiO_2. Only the mineral known as cyanolith, containing lime and silica in a ratio of 1 : 4, is known to be of similar composition. It appears possible that a similar calcium hydrosilicate is formed in the case of Morbelli cement, and that this is capable of bringing its lime content into solution without destroying its mechanical structure. It is possible, also, that steam curing the material hardens it to such an extent that it is very resistant to chemical influences.

Even if insolubility of silica and dilution of cement should prove to be responsible for this improved product, there still remains the fact that artificial ageing of cement can be achieved only if it is mixed with finely ground silica.

Method of Testing Firebricks. By A. Möser (*Tonindustrie-Zeitung*, No. 23, 1934).—Four prisms 1 cm. square in section and 3 to 4 cm. high are cut out of the refractory block under test, placed on a fireclay tile in an electric furnace, and raised to the required temperature. The material under test (such as coal ash, cement, etc.) in powdered form is allowed to pour on to the surface through a tube. In this way a test can be carried out in a few hours.

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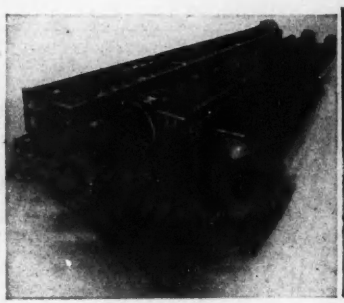

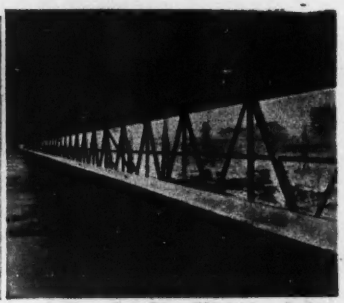

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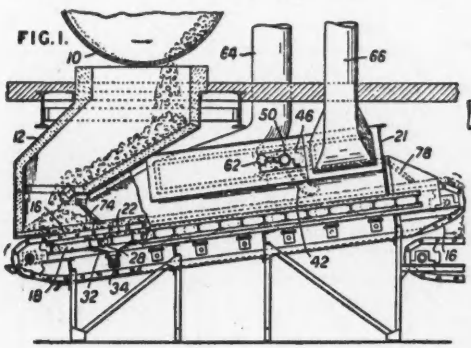
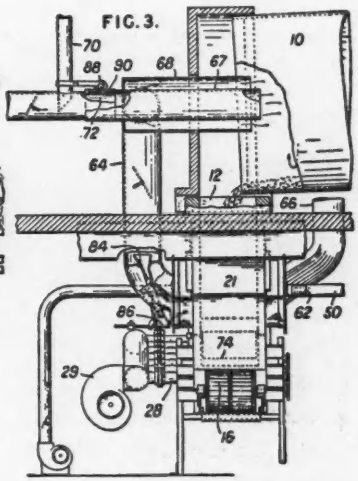
Recent Patents Relating to Cement.

Cement Manufacture.

No. 401,392. Lee, H. S., 2842, West Grand Boulevard, Detroit, Michigan, U.S.A. June 4, 1932.

The clinker produced in a rotary cement kiln (10) is discharged from the latter into a closed chamber (21) in which it is subjected to the action of air supplied through inlets (28) by a fan (29, Fig. 3), pivoted flaps (74, 78) being provided to prevent passage of air to the kiln (10) through the chute (12) and escape of air through the discharge end of the chamber. The clinker discharged at the lower end of the chute (12) first fills a pan (18) to form a bed from which the clinker subsequently discharged is carried into the chamber (21), and along the grate (22) provided therein, by a scraper conveyor (16). The fines falling through the grate (22) are received in hoppers (32) fitted with rotary discharge valves (34). The chamber (21) is divided into two compartments, serving for completion of the burning and for cooling, respectively, by an air-





CEMENT MANUFACTURE.

cooled pivotally mounted partition (42) which carries counterweights (62) and is so arranged that its trunnions (50) may be adjusted longitudinally in the sealed slots (46) to vary the relative capacities of the two compartments. The latter have separate offtakes (64, 66) for the heated air, the former serving to supply secondary combustion air to the kiln (10) while the latter leads to a waste-heat boiler or other heat-exchange apparatus.

White Cement.

406,530.—Nielsen, N., 44, Fuglebakkavej, Frederiksberg, near Copenhagen. May 30, 1933.

In the manufacture of white cement a reducing agent, such as coal, is fed into a rotary kiln near the outlet end, and cooling of the charge is effected within the kiln by supplying a non-oxidising cooling-agent, such as water.

Concretes.

405,508.—Curschellas, J. M., Graubünden, Hanz, Switzerland. (Assignee of Winkler, K., Lugano-Crocifisso, Switzerland.) May 19, 1933.

Hydraulic cements are improved by admixing therewith organic hydroxy acids and/or salts or substitution products thereof such as esters, ethers, and lactones. Acids specified include tartaric, citric, saccharic. They may be dissolved in the gauging water or added to the ground cement or to ground clinker to replace the usual setting regulators, and have a retarding effect. Accelerators and other substances including alkali permanganates, chromates, bichromates, chlorates, other hydraulic cements such as aluminous cement, alkali phosphates, compounds of sesquioxide metals and fluorine or oxalic acid, e.g., potassium-aluminium fluoride, aluminium oxalate, potassium-iron oxalate, and mixtures of alkali aluminate and alkali carbonate, may also be added. In

Patents.—*Continued.*

examples (1) a Portland cement, sand and gravel mix is gauged with 0.18 per cent. solution of saccharic acid; (2) tartaric acid and aluminous cement are added to a mix of Portland cement, sand and gravel; (3) a solution containing potassium carbonate, potassium aluminate, potassium-aluminium fluoride, tartar, and Weldon mud is added to a cement or mortar mix.

Cements.

No. 393,799. Panstwowa Fabryka Zwiazkow Azotowych w Chorzowie, Chorzow, Poland. August 16, 1932.

In the production of phosphorus, ferro-phosphorus, and slag cement, the process is carried out in two stages, the furnace being first charged with a mixture adapted primarily for the production of phosphorus and in the second with a mixture giving a high-grade slag cement and ferro-phosphorus. In the first stage a mixture of phosphates, aluminous material, and coke may be employed, and in the second, aluminous material, limestone or lime, and iron or an iron compound, a higher temperature being employed. In an example, the first charge consists of 100 parts of raw phosphate, 96 of bauxite and 31 of coke, and the second of 100 of bauxite, 38 of lime and 3 of ferric oxide.

Pozzolanic Materials.

No. 394,518. THORNTON, A. A., 7, Essex Street, Strand, London.—(Soc. Anon. Italiana per la Produzione Calci e Cementi di Segni; 262, Corso Umberto 1, Rome.) September 13th, 1932.

A process for increasing the pozzolanic activity of natural pozzolanas, and rocks of volcanic origin, *e.g.*, pozzolana, volcano ashes and tufts, basalts, diabases, trachytes, sienites, gabbros, trasses, Santorin earths, gaizes, molers, etc., consists in heating the material to 400-900° C. and then chilling it, *e.g.*, by air, a mixture of air and steam, or a mixture of air and hydrochloric vapour. The treated material may be mixed in powdered or granulated form with lime or Portland cement to form cements, mortars and concretes.

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